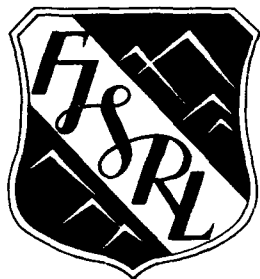


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FRANK J. SEILER RESEARCH LABORATORY

**Viscosity and Conductance
of $\text{MEICl}/\text{AlCl}_3$ Melts
Containing Nonaqueous Solvents**

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**C. J. Dymek, Jr.
and G. E. Godec**

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May 1988

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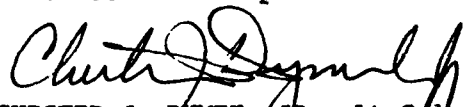
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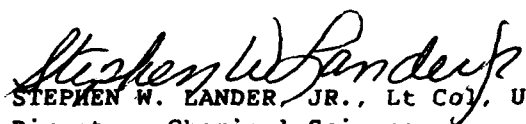
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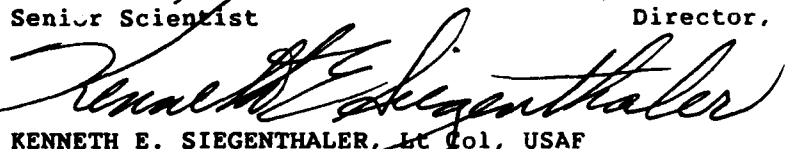
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VISCOSITY AND CONDUCTANCE OF $\text{MEICl}/\text{AlCl}_3$
MELTS CONTAINING NONAQUEOUS SOLVENTS

By

Chester J. Dymek, Jr.

and

Greg E. Godec

May 1988

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Directorate of Chemical Sciences
The Frank J. Seiler Research Laboratory
Air Force Systems Command

TABLE OF CONTENTS

SUMMARY	1
INTRODUCTION	2
EXPERIMENTAL	2
RESULTS AND DISCUSSION	3
REFERENCES	12

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SUMMARY

Ionic liquids formed by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) with AlCl_3 are of interest as electrolytes for batteries. Enhanced conductivities of these melts were observed upon addition of the solvents, benzene, acetonitrile, and dichloromethane. Conductivities and viscosities of these melt/solvent solutions were measured as a function of mole fraction of solvent and found to have similar functional dependence. A model for benzene-ion and ion-ion interactions in the solutions is proposed to explain the variations in the interdependence of conductivity and viscosity in the benzene-melt solutions.

INTRODUCTION

Ionic liquids formed by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) with AlCl_3 are of interest as electrolytes for batteries because they are nonaqueous media with relatively high conductance at and below room temperature (1)(2). It was found that the specific conductance of basic melts (with mole fraction, N , of AlCl_3 less than 0.5) could be increased by the addition of benzene (3). A plausible explanation for this phenomenon is that benzene interacts with the MEI^+ in such a way as to reduce the interionic attractions, thereby making the ions more mobile. The question of whether this is equivalent to an explanation which has the mobility increasing due to decreasing viscosity is the subject of the work reported here. We investigated the dependence of equivalent conductance and fluidity (i.e. inverse of viscosity) on mole fraction of added solvent for three non-aqueous solvents of varying dielectric constant to explore this question.

EXPERIMENTAL

MEICl and AlCl_3 were prepared and purified as previously reported (4). Acetonitrile (OMNI SOLVE grade) was distilled over P_2O_5 for two days. Dichloromethane (Aldrich HPLC grade) was distilled over CaCO_3 for two days. Benzene (Kodak reagent grade) was distilled over CaCO_3 for two days. Melts of MEICl/ AlCl_3 with $N = 0.48$ were prepared in a dry box with a helium atmosphere with less than 10 ppm $\text{H}_2\text{O}/\text{air}$. Melt/solvent solutions were also prepared in the dry box using their weights in closed containers to determine composition. Volumes used to obtain molarity for equivalent conductance determina-

tions were calculated from solution densities. Densities were determined using a Mettler DMA40 Digital Density Meter. Conductances were measured using a YSI model 3402 dips conductivity cell ($k = 1.0 \text{ cm}^{-1}$) inserted in a closed flask containing the solutions of known composition. Measurements were made at 1000 kHz using a YSI Model 31A Conductance Bridge. Kinematic viscosity measurements were made immediately after the conductance measurement had stabilized using a Lauda model B viscometer and KPG-Ubbelode viscometry tubes. Kinematic viscosities were converted to absolute viscosities using the measured densities. All measurements except density were performed in the He-filled dry box at $28 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Equivalent conductances were calculated using the number of moles of MEI^+ as the number of moles of salt present, with AlCl_4^- and Cl^- as the anions. Specific conductances shown in Tables 1, 2, and 3 were recorded after readings had completely stabilized, usually in at least 15 minutes. The viscosities reported are the averages of at least three runs each. The solutions measured were prepared by successive dilutions of the $N = 0.48$ melt with weights measured in closed containers to minimize errors due to solvent evaporation.

Plots of equivalent conductance (in $\text{Scm}^2\text{mol}^{-1}$) and fluidity (in cP^{-1}) vs mole fraction of solvent added to the $N = 0.48$ melts are shown in Figures 1, 2, and 3. The dilutions continued until the appearance of a second phase was observed. For benzene this occurred at about mole fraction of benzene of 0.78 and for dichloromethane, at mole fraction of dichloromethane of 0.90. Acetonitrile was completely miscible with $N = 0.48$ melt at 28°C .

Table 1
Viscosity and Conductance of
MEICl/AlCl₃ Melts Containing Acetonitrile

Mol%	Density	Mol/l	Fluidity	Mol%	Specific Conductance	Equivalent Conductance
0	1.263	4.677	.048	0.0	.0172	3.604
30	1.204	4.456	.118	13.0	.0211	4.574
45	1.182	4.375	.182	26.3	.0256	5.826
50	1.704	4.280	.209	40.3	.0339	8.248
60	1.140	4.218	.299	62.8	.0461	13.659
65	1.265	4.120	.352	72.3	.0588	20.137
70	1.107	4.000	.471	77.0	.0645	24.441
80	1.051	3.890	.679	85.7	.0645	33.247
85	1.011	3.667	.963	89.2	.0690	43.616
90	.951	3.518	1.245	93.0	.0578	51.699
92	.928		1.516	95.1	.0541	65.417
				97.5	.0368	83.070

Table 2
Viscosity and Conductance of MEICl/AlCl₃
Melts Containing Benzene

Mol%	Density g/ml	Specific Conductance	Equivalent Conductance	Fluidity
0.0	1.25	.0185	3.99	.0557
21.7	1.43	.0227	5.28	.0818
39.3	1.21	.0250	6.56	.1199
47.2	1.14	.0272	7.75	.1395
58.0	1.06	.0287	9.29	.1901
71.8	1.00	.0290	12.24	.2882
74.6	0.99	.0279	12.68	.3135
78.0	0.98	.0264	13.33	.3630

Table 3
Viscosity and Conductance of $\text{MEICl}/\text{AlCl}_3$
Melts Containing Dichloromethane

Mol%	Density g/ml	Mol/l [MEI] ^a	Equivalent Conductance	Specific Conductance	Fluidity CP^{-1}
0	1.283	4.765	0190	3.620	0499
30	1.290	4.225	.0227	5.386	.0951
45	1.293	3.817	0270	7.079	1398
60*			.0323	9.835	
65*			.0331	10.681	
65	1.309	3.088	.0330	10.687	.2603
67*			.0332	11.455	
70	1.310	2.794	0332	11.891	.3122
70*			.0333	11.903	
72*			.0333	12.808	
75*			.0333	13.660	
75	1.317		.0323	13.658	.3691
78*			.0331	14.716	
80	1.318	2.164	.0323	14.935	.4626
85	1.319	1.757	.0296	16.842	.6158
90	1.319	1.276	.0226	17.727	.8970

^aSecond data set

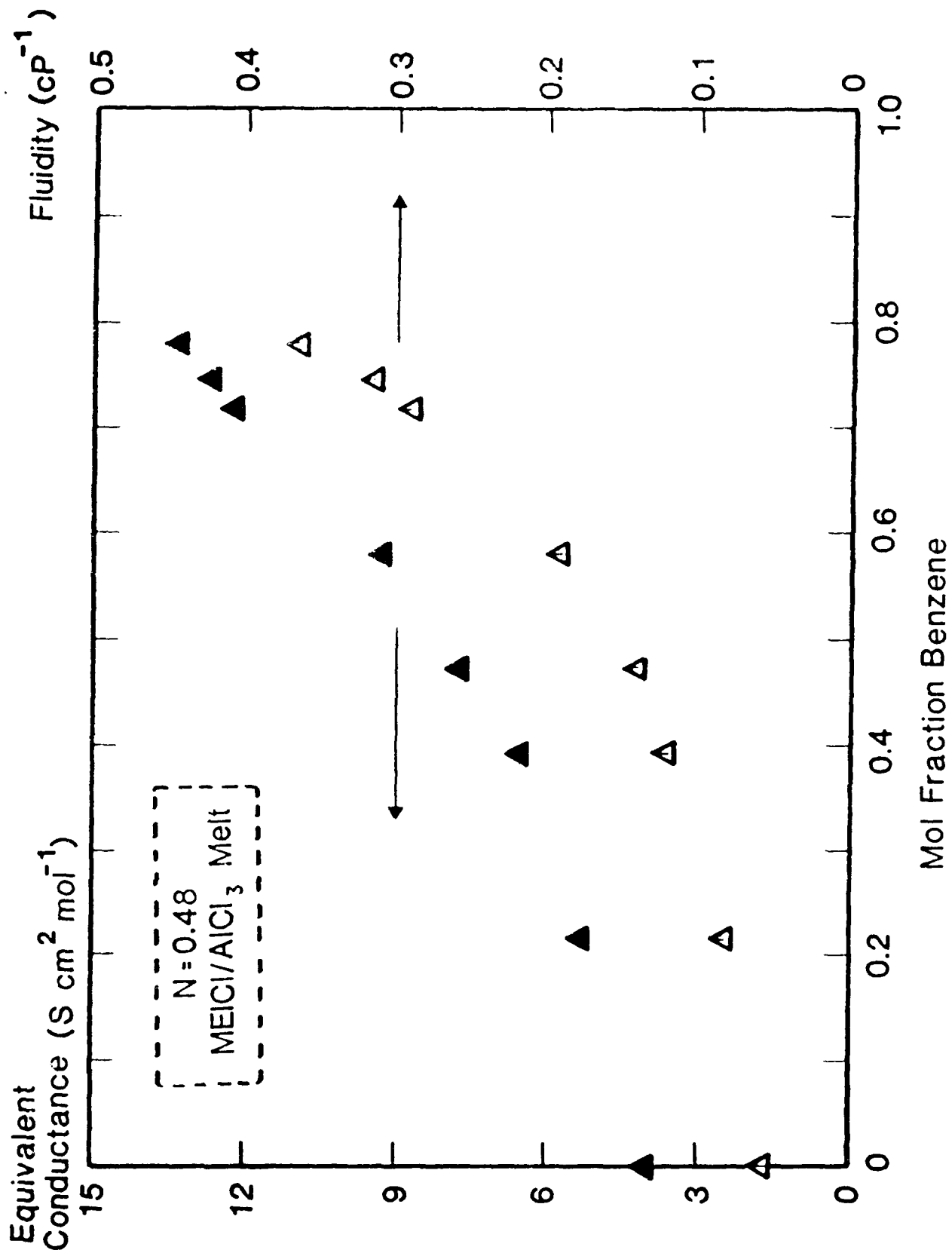


Figure 1. Equivalent Conductance and Fluidity of $N=0.48$ Melt as a Function of Mol Fraction of Added Benzene.

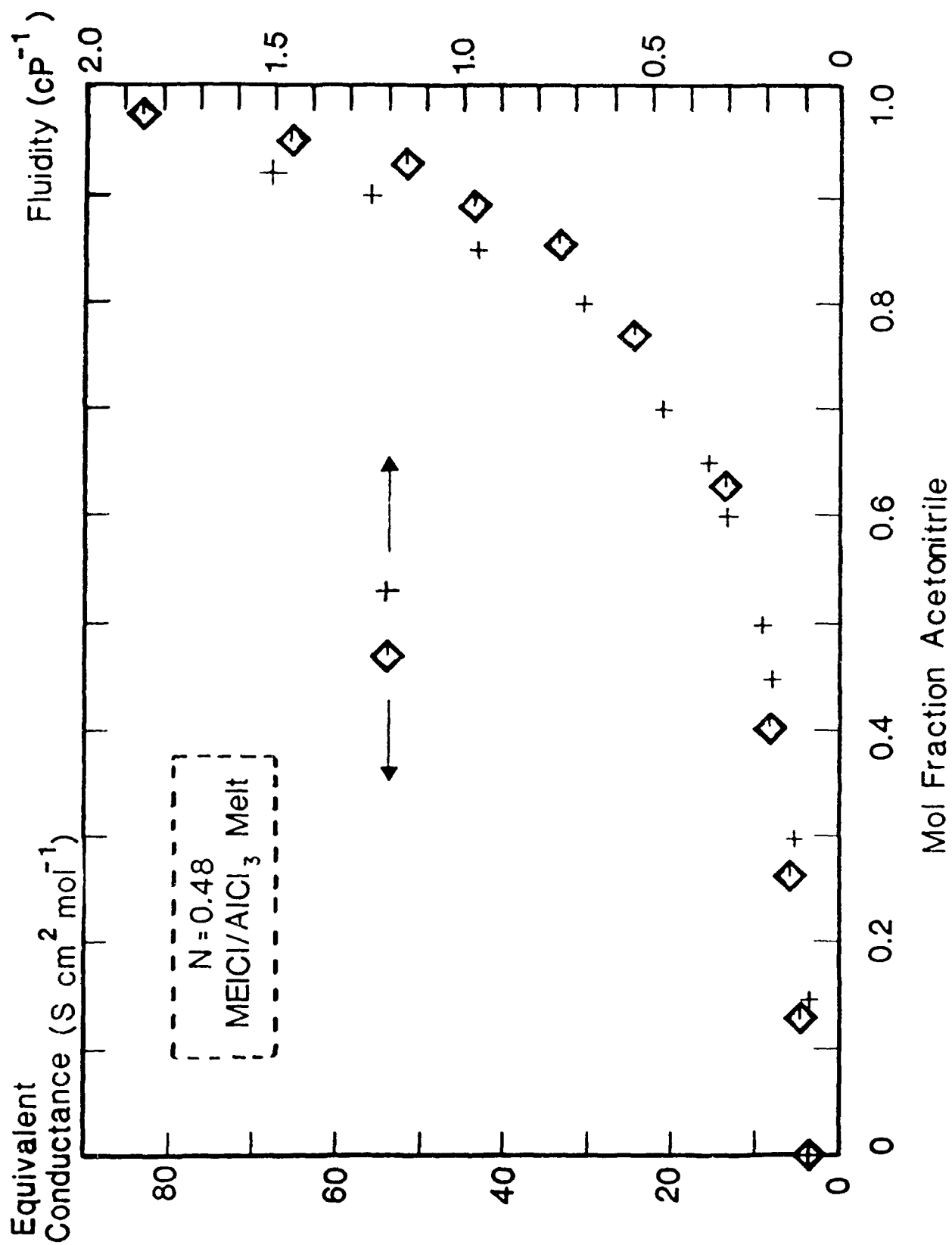


Figure 2. Equivalent Conductance and Fluidity of $N=0.48$ Melt as a Function of Mol Fraction of Added Acetonitrile.

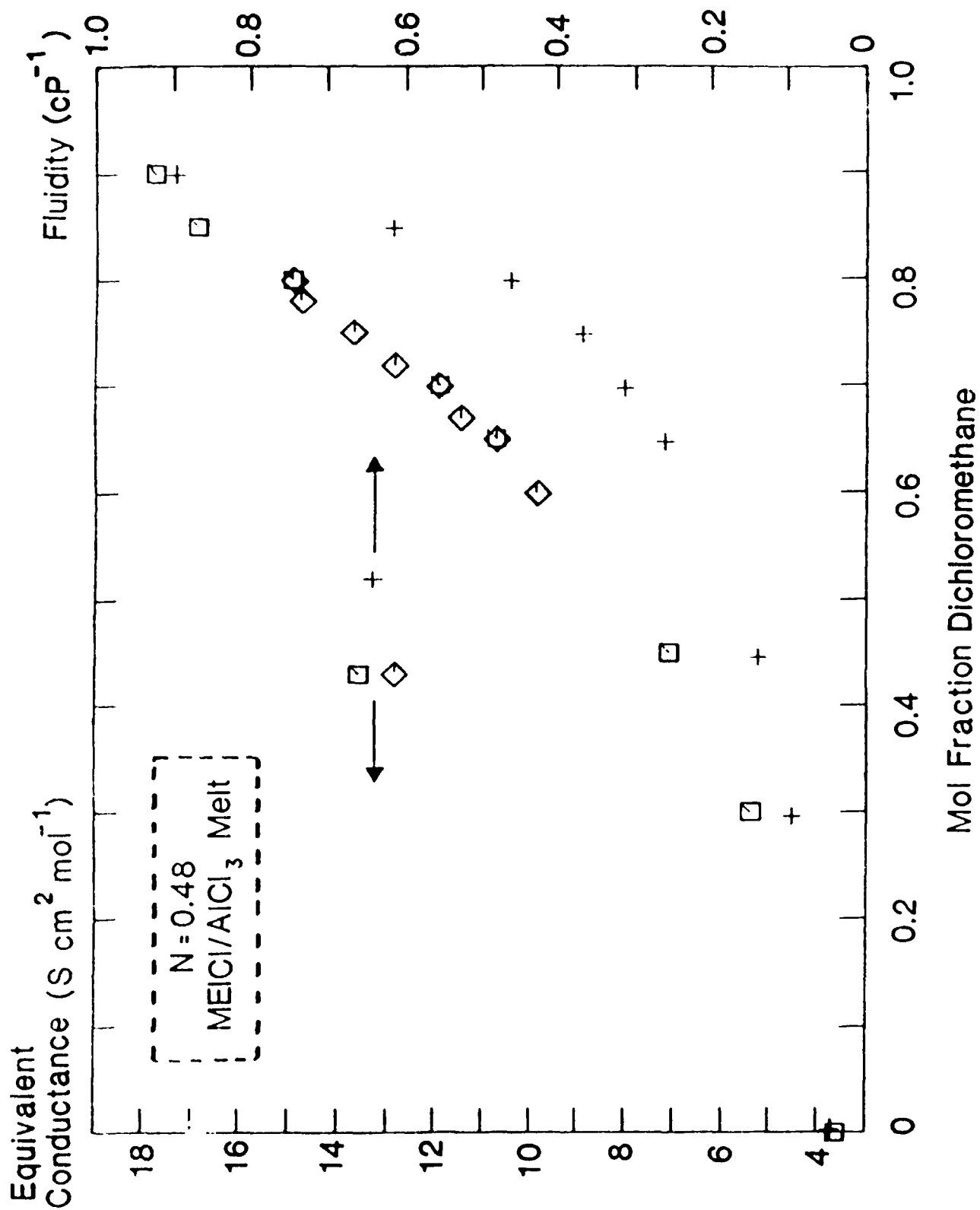


Figure 3. Equivalent Conductance and Fluidity of $N=0.48$ Melt as a Function of Mol Fraction of Added Dichloromethane.

Over the range of mole fraction of solvent added in which they can be compared, there is little difference in the fluidity or equivalent conductances for the three solutions. What is clear from the results is that the equivalent conductance has very nearly the same functional dependence on mole fraction of solvent added as does the fluidity. Dichloromethane shows the most obvious deviation from this behavior, an observation which prompted a second run for this system as shown in Figure 3. In benzene and dichloromethane solutions, as the limit of miscibility is approached, the equivalent conductance curve starts to turn over relative to the fluidity curve. This suggests that the formation of ion pairs or clusters of ion pairs is beginning to occur as this limit is reached. However, it is clear that the viscosity of the solutions is the primary factor determining the equivalent conductance over most of the range of miscibility. Thus the increased conductivity of melts with these solvents added can be attributed primarily to their increased fluidity. This in turn is attributable to the breaking up of strong interionic attractions by the added solvents. How these solvents "solvate" the MEI^+ , Cl^- , and AlCl_4^- ions is the subject of other ongoing work in this laboratory.

We now propose a model of what is occurring in the melt as benzene is added. In Figure 4, benzene and MEI^+ are both shown only in end-on positions to simplify the drawings and to emphasize how benzene and MEI^+ interact. Of course, in a melt the orientations of both would be random, although some transitory short-range structure surely exists. The saw-toothed lines represent attractive interactions between ions. The four stages shown in Figure 4 are briefly described:

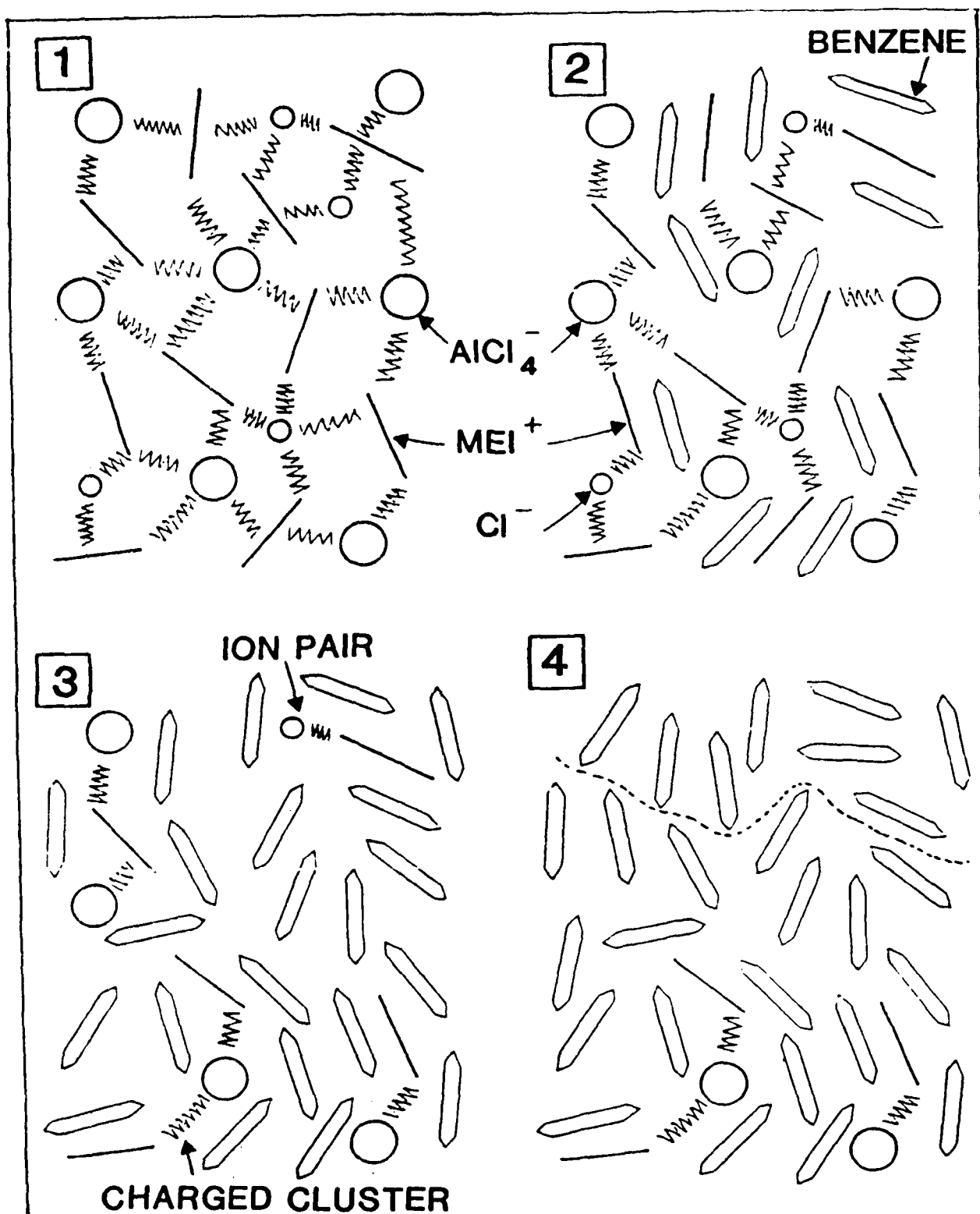


Figure 4. Proposed Model Showing Effect of Added Benzene on Melt Equivalent Conductivity and Fluidity.

1. With no benzene present, the mobility of the ions is limited by the attractive forces they experience from the extended ionic cage which surrounds them. Both fluidity and equivalent conductance are at a minimum.

2. At low concentrations of benzene, the benzene molecules "solvate" the MEI^+ ions whose interactions with surrounding anions are therefore reduced, leading to increased mobility of both MEI^+ and the anions. Thus both fluidity and equivalent conductance increase.

3. After two benzene molecules for each MEI^+ present have been added (mol fraction benzene of 0.67), additional benzene is now solvating not just MEI^+ but also ion-pairs or neutral clusters of ion-pairs as well as charged clusters. This process reduces the number of charge carriers available in the melt solution while at the same time it continues to reduce interactions between ions or charged clusters of opposite charge. Thus the equivalent conductance begins to decrease due to the reduced number of charge carriers even though fluidity increases due to the reduction in interionic attractions.

4. Finally a point is reached at which additional benzene is shielded from interaction with MEI^+ or other benzene molecules which are solvating MEI^+ . The normal intermolecular forces of pure benzene force this additional benzene into a second phase as indicated by the dashed line in Figure 4.4.

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